University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part A

Faculty of Engineering and Information
Sciences

1-1-2014

Effects of tungsten on the hydrogen embrittlement behaviour of microalloyed steels

Jingwei Zhao

University of Wollongong, jzhao@uow.edu.au

Zhengyi Jiang

University of Wollongong, jiang@uow.edu.au

Chong Soo Lee

Pohang University of Science and Technology, cslee@postech.ac.kr

Follow this and additional works at: <https://ro.uow.edu.au/eispapers>

Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Effects of tungsten on the hydrogen embrittlement behaviour of microalloyed steels

Abstract

The effects of tungsten (W) additions (0, 0.1, 0.5 and 1 wt.%) on the hydrogen embrittlement behaviour of microalloyed steels were systematically investigated by means of slow strain rate tests on circumferentially notched cylindrical specimens, and the mechanism of hydrogen-induced embrittlement was discussed. W addition is found to increase the activation energy of hydrogen desorption. Microstructural features affect the hydrogen embrittlement behaviour and fracture modes of microalloyed steels. It is suggested that the hydrogen-induced embrittlement in the studied microalloyed steels with different W additions is caused by the combined effects of decohesion and internal pressure in the presence of hydrogen.

Keywords

tungsten, hydrogen, embrittlement, behaviour, effects, microalloyed, steels

Disciplines

Engineering | Science and Technology Studies

Publication Details

Zhao, J., Jiang, Z. & Lee, C. Soo. (2014). Effects of tungsten on the hydrogen embrittlement behaviour of microalloyed steels. *Corrosion Science*, 82 380-391.

Effects of tungsten on the hydrogen embrittlement behaviour of microalloyed steels

Jingwei Zhao¹, Zhengyi Jiang¹, Chong Soo Lee^{2,*}

¹School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, NSW 2522, Australia

²Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

Abstract

The effects of tungsten (W) additions (0, 0.1, 0.5 and 1 wt.%) on the hydrogen embrittlement behaviour of microalloyed steels were systematically investigated by means of slow strain rate tests on circumferentially notched cylindrical specimens, and the mechanism of hydrogen-induced embrittlement was discussed. W addition is found to increase the activation energy of hydrogen desorption. Microstructural features affect the hydrogen embrittlement behaviour and fracture modes of microalloyed steels. It is suggested that the hydrogen-induced embrittlement in the studied microalloyed steels with different W additions is caused by the combined effects of decohesion and internal pressure in the presence of hydrogen.

Keywords: A. Low alloy steel; B. Hydrogen permeation; C. Hydrogen absorption; C. Hydrogen embrittlement

* Corresponding author. Tel.: +82-54-279 2141; fax: +82-54-279 2399

E-mail addresses: jwzhaocn@gmail.com (J. Zhao), jiang@uow.edu.au (Z. Jiang), cslee@postech.ac.kr (C.S. Lee)

1. Introduction

Microalloyed steel, which is also called high-strength low-alloy (HSLA) steel, is a category of alloy steel that contains small amounts of alloying elements such as titanium (Ti), niobium (Nb) and vanadium (V) etc. The addition of alloying elements in microalloyed steels plays a key role in the grain size refining and precipitation hardening [1]. Microalloyed steels offer increased excellent mechanical properties at a moderate increase in price over carbon steels, and they are economical for a variety of applications such as cars, trucks, bridges, oil and gas extraction, construction equipment, off-highway vehicles, mining equipment and other heavy-duty structures [2,3]. Microalloyed steels have been developing rapidly over the past several years, and extensive investigations have been conducted with a view of improving the toughness and strength in order to meet the requirement of excellent mechanical properties for various practical applications [4-7]. Tungsten (W) is a strong ferrite former, and is effective for precipitate refining and solid solution strengthening. W is usually added to steels as an alloying element to improve their mechanical properties, and several attempts have been made to achieve this goal in tool steels, high speed steels, heat resisting steels and stainless steels, and steels used in power-generation and chemical industries [8-13]. For microalloyed steels however, only limited published work is available with regard to W alloying in them. Our previous studies have indicated that W addition in microalloyed steels changes the phase transformation characteristics [2] and influences the microstructural evolution behaviour [3,14]. The addition of proper amount of W is beneficial for the improvement of room/low temperature tensile strength and ductility of microalloyed steels [15]. W alloying in microalloyed steels is becoming a rear and fruitful research field.

One of the significant challenges in the development of high strength steels is the so-called hydrogen embrittlement (HE) when these steels are applied in a hydrogen environment. It has been found that high strength steels are susceptible to HE, and the susceptibility to HE increases with enhancing the strength level [16,17]. The ductility will decrease and an unpredictable failure may

occur in the presence of hydrogen in steels [18,19]. Numerous studies on the HE of high strength steels have been carried out in various environments such as stress corrosion cracking in an aqueous or H₂S and charging in H₂ gas or an aqueous solution in order to understand well the mechanism of hydrogen induced failure of these steels [20-29]. It is generally accepted that HE of steels correlates closely with the attractive interactions between hydrogen atoms and structural imperfections in crystals, i.e. the hydrogen trapping phenomena at various structural imperfections in steels affect the susceptibility of hydrogen-induced embrittlement [30]. The presence of hydrogen in solution in steels is mainly related to the small diameter of hydrogen atom and its capacity to diffuse and/or trap under a certain condition in solid state. Different factors such as environment, temperature, chemical composition, stress status and microstructural constituents can affect the hydrogen diffusion and trapping behaviour in steels [31]. It has been found that almost all kinds of defects in steels including vacancies, dislocations, interfaces, micro-voids and grain boundaries can act as hydrogen trapping sites [30,32]. The trapped hydrogen may diffuse to the stress-concentrated zone and microcracks that occurred at the tips of defects during loading, and an early failure is expected as the loading proceeds. There are generally two kinds of hydrogen trapping sites in iron and steels based on the trapping activation energy that is needed to escape from the trapping site to the normal lattice site. **Table 1** presents the values of trapping activation energies for a number of trapping sites in iron and steels. It can be seen that the trapping activation energies of hydrogen for defects like iron lattice, grain boundary, austenite/martensite interface, dislocation, austenite/dislocation boundary, microvoid and Fe oxide interface are low, while those for ferrite/cementite interface and various non-metallic inclusions such as Cr carbide, Y₂O₃, MnS, Al₂O₃, Fe₃C and a precipitate, TiC are high. The ferrite/cementite interface and interfaces of non-metallic inclusions with high trapping activation energy of hydrogen are usually called irreversible trapping sites, whereas those with lower energies are termed as reversible or diffusible trapping sites [17,30].

Due to the harmful effect of HE in high strength steels, an insight in the interaction between

hydrogen and failure behaviour is of crucial importance. Extensive investigations have been performed to understand the causes of HE occurring in various high strength steels, such as twining-induced plasticity (TWIP) steel [46], transformation induced plasticity (TRIP) steel [47], dual phase (DP) steel [48], high Mn steel [36], tempered martensitic steel [31], ferrite-martensite steel [49], stainless steel [50], maraging steel [50] and ODS RAF steel [17]. With regard to the HE occurred in microalloyed steels, Michler and Naumann [19] performed heat treatments on some microalloyed steels with different chemical compositions in order to obtain a variety of microstructural combinations of ferrite/pearlite, bainite and martensite. Tensile tests on smooth specimens of these steels were then conducted in a gaseous hydrogen environment at room temperature. They found that hydrogen assisted crack propagation, and hydrogen enhanced localised plasticity was the primary failure mechanism. Increased acicular ferrite content in the microstructure improved the resistance of hydrogen-induced cracking in the welded API 5L-X70 microalloyed pipeline steels, and the precipitated titanium carbonitrides could act as beneficial hydrogen traps and delay cracking in hydrogen sulphide environment [51]. The work of Kim et al. [52] indicated that hydrogen induced cracking in microalloyed steels primarily nucleated at inclusion and/or clusters containing the Al and Ca oxides. Kim et al. [53] concluded that in acicular ferrite, Fe_3C particles acting as reversible trapping sites for hydrogen atoms were newly precipitated along the grain boundary of microalloyed steel by the post-weld heat treatment at 620 °C. This led to an increase in diffusible hydrogen content in the steel that made it more susceptible to hydrogen-induced cracking. Nanninga et al. [54] studied three microalloyed pipeline steels by tensile tests in a high-pressure hydrogen gas environment. The results indicated that hydrogen absorption occurred prior to reaching the yield point for these steels, but after yielding, the rate of absorption and diffusion became much more rapid due to dislocation assisted mobility. They concluded that this initial hydrogen probably led to the formation of the hydrogen-induced surface cracks, and the tensile specimens tested in hydrogen failed through a mechanism of surface crack initiation and growth that occurred during the necking of the tested specimens. The micro-mechanism of hydrogen cracking was quasi-cleavage fracture of ferrite grains.

Alp et al. [55] found that the susceptibility to HE in microalloyed steel was closely related to the microstructural state. Hydrogenated specimens with martensite islands in a ferrite matrix basically exhibited quasi-cleavage fracture with some ductile dimpling. The mode of fracture in charged specimens quenched from higher intercritical annealing temperatures was predominantly intergranular fracture along prior austenite grain boundaries and cracking of martensite laths. Although HE of microalloyed steels has been investigated extensively, there is still no relevant publication available that addresses HE behaviour in W-containing microalloyed steels, let alone a systematic investigation on the quantitative relationships among hydrogen concentration, W content and HE behaviours. As an alloying element with growing scientific and industrial interests, W has attracted an increasing attention due to its positive effect in microalloyed steels. It is therefore worthwhile to conduct an in-depth research with the purpose of understanding the effects of W on the HE behaviour of microalloyed steels. The research has practical applications, and the outcomes will be helpful in the development of W-containing microalloyed steels.

In the current study, several microalloyed forging steels with varying W contents were produced by a controlled forging process. This work aims to systematically investigate the HE behaviour of microalloyed steels with different W additions. The trapping activation energies of hydrogen in the W-containing microalloyed steels were quantified. The relationship between hydrogen concentration and tensile properties was investigated, and the effects of hydrogen on the fracture behaviour were analysed. In addition, the mechanism of hydrogen-induced embrittlement in the microalloyed steels with different W contents was discussed.

2. Experimental procedure

2.1. Materials

Four microalloyed forging steels with different W contents were adopted in this study. The chemical compositions are summarised in **Table 2**. The addition of W was intended to modify the

microstructure and improve the mechanical properties of microalloyed forging steels. Room temperature tensile tests were carried out at a strain rate of $5 \times 10^{-3} \text{ s}^{-1}$ on the specimens with a gauge length of 30 mm and gauge diameter of 6 mm according to ASTM E 8M. The values of hardness were measured with a Vickers hardness tester using 2 kg load and 10 s dwell time, and 8 indentations for every specimen were made randomly on its surface. The mechanical properties are listed in **Table 3**. Since the fabrication of these microalloyed steels, and the microstructural evolution and mechanical properties variation after W addition have been detailed in our previous study [15], the current work will focus on the HE behaviour of these steels.

2.2. Hydrogen charging

Circumferentially notched cylindrical specimens with a notch section diameter of $\Phi=6$ mm, a notch angle of $\theta=60^\circ$ and a notch root radius of $R=0.1$ mm were machined for slow strain rate test (SSRT). The detailed dimensions and the appearance of a notched specimen are shown in **Fig. 1**. The notched specimens were prepared by a computerised numerical control (CNC) machine. The stress concentration factor was 4.9 [16]. Local stress concentration will be caused at the notch during tensile deformation. Several studies have indicated that notch accelerates the diffusion of hydrogen from other zone to the notch root, and therefore helps to increase the hydrogen mobility in the specimens during loading [56,57].

Hydrogen was introduced into the notched specimens by electrochemical charging in a solution of “3 wt.% NaCl + 0.3 wt.% NH_4SCN ” under the current densities of 1 to 20 A/m^2 for 48 h at room temperature. The roles of Na^+ and Cl^- ions in the solution are electrolytes and the acid hydrolysis of NH^+ supplies H^+ ions, which remain as adsorbed atoms on the specimen surface after cathodic reduction. The recombination of H^+ ions into a gaseous form is inhibited by the CNS^- ions [58]. Due to the sensitivity of hydrogen charging to the surface roughness, all the surfaces of the notched

specimens were mechanically polished with #1200 SiC sand papers before hydrogen charging processes.

Immediately after hydrogen charging, the specimens were mechanically polished with #1200 SiC sand papers and then electroplated with a cadmium (Cd) coating to prevent hydrogen desorption. Cd-coated layer is also an effective barrier to hydrogen escape from the specimens during the subsequent SSRTs. For Cd coating, specimens were connected to the cathode of the power, and then they were inserted into a mixed electrolyte solution of “ $\text{Cd}(\text{BF}_4)_2 + \text{NH}_4\text{BF}_4 + \text{H}_3\text{BO}_4 + \text{water}$ ”. Cd metal block put in this electrolyte solution was connected to the anode of the power. Coating time was controlled to be 5 min for a hydrogen-charged specimen under the current of 0.5 A. Following Cd coating, the specimens that were hydrogen charged for 48 h were kept at ambient for 24 h to homogenise the hydrogen distribution. Previous experimental study has indicated that a total time of 72 h for charging and homogenising is effective and reasonable for obtaining uniformly-distributed hydrogen in the specimens [59]. Then, the specimens were subjected to SSRTs.

2.3. SSRT and thermal desorption spectrometry (TDS) analysis

SSRT was performed on an INSTRON 8501 tensile testing machine at a constant stroke speed of 0.005 mm/min (strain rate is $8.3 \times 10^{-7} \text{ s}^{-1}$). The Cd-coated layer was electrochemically removed from the specimen surface immediately after SSRT. The process for removing Cd from the specimen surface is similar to that of Cd coating. The only difference is that specimen should be connected to the anode, and Cd metal block should be connected to the cathode of the power during the removal process of the Cd-coated layer. The average hydrogen concentration in a hydrogen-charged specimen was evaluated by means of TDS analysis using a gas chromatography (Agilent GC 7890A) at a heating rate of 100 K/h. The temperatures were raised from ambient temperature to 773 K to obtain different hydrogen desorption profiles. During TDS analysis, the emitted gas was collected at an interval of 5 min under a continuous helium gas flow. The total hydrogen that was desorbed below

600 K during heating was regarded as the diffusible hydrogen because it can diffuse out of the specimens if the specimens are exposed at room temperature. In addition, this hydrogen is essential for the occurrence of hydrogen-induced embrittlement, although it would be either lattice hydrogen or weakly trapped hydrogen [16]. The hydrogen trapping sites were identified based on the activation energy of hydrogen desorption. Other heating rates of 200 K/h and 300 K/h were also employed for determining the activation energy of hydrogen desorption.

2.4. Metallography and fractography

Metallographic specimens were etched with 2% nital solution for microstructural observation by an OLYMPUS BX51M optical microscope (OM). To examine the characteristic of precipitates, extraction replicas as well as thin foils mounted on Cu grids specimens were prepared and analysed on JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV. The fracture surfaces of the tested specimens were observed on SEM using an accelerating voltage of 15 kV to determine the failure mode.

3. Results

3.1. Microstructural characterisation

Fig. 2 presents the microstructures of all the tested steels. The 0W steel is mainly composed of polygonal ferrite (PF) and pearlite, accompanied by a small quantity of acicular ferrite (AF), as shown in **Fig. 2a**. The addition of W has significantly changed the microstructures. As shown in **Fig. 2b**, the amount of AF increases after 0.1% W addition compared with the 0W steel. As the W content is increased to 0.5%, a remarkable increased amount of AF encircled by allotriomorphic ferrite is observed (**Fig. 2c**). Allotriomorphic ferrite is the first phase to form on cooling the austenite grains below the austenite to ferrite equilibrium transformation temperature. It nucleates at the columnar austenite grain boundaries. Because these boundaries are easy diffusion paths, they become decorated with continuous layers of ferrite [3]. With continuously increasing W content from 0.5% to 1%, the

microstructure becomes a mixture of AF and bainite, as indicated in **Fig. 2d**. The mechanism of W-induced microstructural evolution of microalloyed steels is detailed in our previous work [15].

3.2. Hydrogen desorption and trapping

Fig. 3 shows the typical hydrogen desorption curves of the 0W steel. As shown in **Fig. 3a**, no hydrogen desorption curve appears during heating for the uncharged specimen. The hydrogen-charged specimens, however, exhibit additional hydrogen desorption peaks at a temperature of around 360 K, which are undoubtedly caused by hydrogen charging. The magnitude of the peak desorption rate indicates the amount of charged hydrogen in the specimen, and a higher peak corresponds a higher hydrogen concentration. Under the charging current densities of 5 and 10 A/m², for example, the measured hydrogen concentrations are 0.55 and 0.98 mass ppm, respectively, by means of TDS analysis. **Fig. 3b** illustrates the effects of heating rate on the hydrogen desorption curves. It is clear that the higher the heating rate during TDS analysis, the higher the temperature to the peak desorption rate is expected.

Fig. 4 shows the effects of W on the profile of hydrogen desorption curves. It can be seen that the peak values decrease gradually with the increase of W, and the peak shifts to a higher temperature side as W is added. W addition induces a reduced peak area (an area underneath the hydrogen desorption curve). The peak area is proportional to the hydrogen concentration that charged in a specimen [46]. Under the charging current density of 5 A/m², the measured hydrogen contents are 0.55, 0.52, 0.48 and 0.42 mass ppm, for the 0W, 0.1W, 0.5W and 1W specimens, respectively. Therefore, W addition decreases the amount of diffusible hydrogen in microalloyed steels under the same hydrogen charging current density.

The dependence of measured hydrogen concentration on charging current density of the tested steels is illustrated in **Fig. 5**. It is clear that the hydrogen concentration increases with charging current

density for all the specimens. Under a given charging current density, the hydrogen concentration shows a decreasing trend with the increase of W, which is consistent with the result obtained from **Fig. 4**. It is therefore more difficult for hydrogen to permeate in W-added steels during hydrogen charging relative to the 0W steel.

Hydrogen in steel is prone to be trapped at various structural defects such as dislocations and grain boundaries. To identify the hydrogen trapping sites, the activation energy of hydrogen desorption is calculated by the Kissinger [60] equation as:

$$\frac{\partial \ln(\phi/T_p^2)}{\partial(1/T_p)} = -\frac{E_a}{R} \quad (1)$$

where ϕ is the heating rate in K/s, T_p is the peak temperature in K, E_a is the activation energy of hydrogen desorption in kJ/mol, and R is the gas constant. After performing TDS analysis using different heating rates (100, 200 and 300 K/h in the current work) and the determination of the corresponding peak temperatures for a trap in the hydrogen desorption curves, the slope of $\ln(\phi/T_p^2)$ versus $(1/T_p)$ plot allows to obtain the value of E_a that corresponds to a specific hydrogen trapping site. The activation energies of hydrogen desorption are calculated to be 12.75, 16.19, 21.57 and 25.82 kJ/mol for the 0W, 0.1W, 0.5W and 1W steels, respectively, based on Eq. (1). Our previous study has indicated that the dislocation density increases gradually with increasing the W content from 0 to 1% in the microalloyed steels [15]. According to **Table 1**, the calculated E_a in both the 0W and 0.1W steels should correspond to the hydrogen in lattice and trapped by reversible trapping sites such as grain boundaries and dislocations [16]. The measured diffusible hydrogen in the 0.5W steel is probably trapped by grain boundaries and dislocations since the activation energy and peak temperature are very similar to the reported ones [59,61]. The E_a value for the 1W steel, 25.82 kJ/mol,

makes us believe that the hydrogen may be trapped in dislocations, which is consistent with the result ($E_a \approx 26.8$ kJ/mol) obtained by Choo and Lee [34].

3.3. Notch tensile behaviour

As indicated in **Fig. 5**, the hydrogen concentrations are different in the steels with different W additions even though under the same hydrogen charging current density. In the present work, the notch tensile behaviour of the steels with different hydrogen concentrations will be evaluated only under different hydrogen charging current densities, while the corresponding real hydrogen concentrations can be obtained directly from **Fig. 5**. **Fig. 6** shows the tensile stress versus displacement curves of the notched specimens that were charged under different hydrogen charging current densities. In the figure, A0 indicates the specimen that was uncharged, and A1, A5, A10 and A20 represent the specimens that were charged under current densities of 1, 5, 10 and 20 A/m², respectively. For the 0W steel, all the specimens show yielding and necking behaviour before final fracture, and the ultimate notch stress and the displacement to fracture (D_f) decrease gradually with the increase of current density (**Fig. 6a**). After 0.1% and 0.5% W additions, the specimens without hydrogen charging exhibit a similar notch tensile behaviour to that of the 0W steel. Differently, the notch stress shows an increasing trend with the increase of W content, and the displacement to fracture is reduced after W addition, as shown in **Fig. 6b and c**. The hydrogen-charged specimens exhibit an early fracture before obvious yielding, and the higher the current density, the earlier the fracture occurs. The addition of 1% W has significantly changed the notch tensile behaviour. As shown in **Fig. 6d**, fracture occurs before an ultimate notch stress is obtained for all the tested specimens. When the current density reaches 10 A/m² or a much higher value, the curve of the 1W steel appears to be a straight line, which means no obvious yielding and necking behaviour is observed before the final fracture occurs (**Fig. 6d**). In addition, there is no significant change in the slope of notch tensile curve with varying W contents and hydrogen charging current densities,

indicating both W and hydrogen have no significant effect on the elastic deformation before the final fracture occurs.

Fig. 7 shows the variations of fracture stress (σ_f) and D_f with W content under different hydrogen charging current densities. As shown in **Fig. 7a**, the σ_f of the uncharged specimens increases gradually at first, then to a maximum value at the W content of 0.5%, and finally it drops slightly when the W content is higher than 0.5%. The values of σ_f are reduced from 774.6 to 735.0, 1028.2 to 837.1, 1086.8 to 820.8, and 1065.2 to 688.8 MPa for the 0W, 0.1W, 0.5W and 1W steels, respectively, after hydrogen charging under current density of 1 A/m². The drop of σ_f shows an increasing trend with W, as indicated by the arrows in **Fig. 7a**. Among the hydrogen-charged specimens, the σ_f increases after 0.1% W addition, and then it decreases slightly when the W content reaches 0.5%. When the W content is increased to 1%, a sharply decreased σ_f is observed. As shown in **Fig. 7b**, the D_f of the uncharged specimens shows a decreasing trend with W. The arrows in **Fig. 7b** indicate that hydrogen charging induces significant reduction of D_f , and the drop of D_f decreases gradually with W. Moreover, the greater the current density, the smaller the values of σ_f and D_f are expected. Based on **Figs. 5 and 7**, it can be concluded that both σ_f and D_f exhibit a decreasing trend with the increase of hydrogen concentration because the charged hydrogen concentration increases with current density.

3.4. Fractography

Fig. 8 shows the fracture surfaces of the notched 0W specimens with and without hydrogen charging. At low magnification, the fracture characteristics of both the charged and uncharged specimens along the notch roots are observed to be somewhat different from that in other locations (**Fig. 8a and b**). Observations on the uncharged specimen at a higher magnification show that a ductile fracture region (width is about 610 μm) which is composed of small dimples exists in the vicinity of the notch root (**Fig. 8c**), while full cleavage fracture occurs in the central zone (**Fig. 8e**). Also, the depth of dimples shows a decreasing trend along the direction from the margin of the notch

root to the centre, and an immediate cleavage fracture is caused beyond the ductile fracture region from the notch root, which presumably corresponds to the crack initiation at the notch root and propagation towards to the central region till a final cleavage fracture is caused. Hydrogen charging has significantly changed the fracture mode of the tested specimen. As shown in **Fig. 8d**, the hydrogen-charged specimen exhibits a brittle quasi-cleavage fracture in the vicinity of notch root. Comparing **Fig. 8c and d**, the width and the location of the quasi-cleavage region are found to be same as that of the uncharged specimen, indicating a ductile to quasi-cleavage fracture transition of the 0W steel has taken place after hydrogen charging under current density of 1 A/m^2 . In addition, hydrogen charging does not show noticeable effect on the fracture mode in the central zone, i.e. the hydrogen-charged specimen still exhibits a full cleavage fracture feature in the central zone which is characterised to be the same mode as the uncharged specimen, as compared in **Fig. 8e and f**.

Fig. 9 shows the fracture surfaces of the notched 0.1W and 0.5W specimens that were uncharged and hydrogen-charged under current density of 1 A/m^2 . The fracture surfaces of the uncharged 0.1W and 0.5W specimens exhibit a similar characteristic to that of the 0W specimen, i.e. both the fracture surfaces are composed of a ductile fracture region near the notch root and a full cleavage fracture region in other locations. By comparing **Figs. 8c, 9a and 9c**, it can be found that the ductile fracture region is reduced after W addition, and the greater the W content, the narrower the ductile fracture region is observed. The ductile fracture occurred in the vicinity of the notch root turns to be quasi-cleavage fracture after hydrogen charging, as indicated in **Fig. 9b and d**. This finding is consistent with the result obtained from **Fig. 8** that hydrogen benefits the ductile to quasi-cleavage fracture transition and thus promotes the occurrence of embrittlement in microalloyed steels with and without W additions.

Fig. 10 presents the fracture surfaces of the notched 1W specimens with and without hydrogen charging. As shown in **Fig. 10a**, no ductile fracture region is observed on the uncharged specimen,

and a full cleavage fracture has been caused after 1% W addition. Hydrogen does not show significant change in the fracture morphology, and the fracture feature of the hydrogen-charged specimen still shows a full cleavage mode, as shown in **Fig. 10b**.

The fracture surfaces have been changed as the current density increases. As shown in **Fig. 11**, quasi-cleavage fracture still occurs in the vicinity of notch root of the 0W specimen after hydrogen charging under current density of 10 A/m². Differently, the width of the quasi-cleavage region has been decreased as the current density is increased from 1 to 10 A/m², as indicated in **Figs. 8d and 11**. **Fig. 12** shows the fracture surfaces of the W-containing specimens that were hydrogen-charged under current density of 10 A/m². Two distinct fracture regions, i.e. a quasi-cleavage fracture region in the vicinity of the notch root and a full cleavage fracture region in other locations, are found on both the 0.1W and 0.5W specimens, as shown in **Fig. 12a through d**. Small amounts of microcracks are observed at the edge of the notch root of the 0.1W specimen, as shown in **Fig. 12a and b**. The characteristic and quantity of microcracks have been changed when the W content increases. As indicated in **Fig. 12c and d**, large numbers of through microcracks along the margin of the notch root are found as the W content is increased from 0.1 to 0.5%. For the 1W specimen, however, the fracture surface shows a full cleavage mode, and no microcrack is found along the notch root, as shown in **Fig. 12e and f**.

4. Discussion

The permeability of hydrogen in steels is affected by the microstructural features including phase constituents, grain boundaries, grain size and shape, vacancies and dislocations, interfaces with non-metallic inclusions, precipitate particles and voids [62,63]. The work of Wang et al [64] indicated that the main diffusion paths for hydrogen were the grain boundaries of equiaxed ferrite and ferrite/carbide interfaces of pearlite in the ferrite/pearlite steel, ferrite/carbide interfaces of long needle-like or lath-like bainite in bainitic steel, and boundaries of the blocky grain boundary ferrite and interfaces in the

steel with AF structure. They concluded that the permeability and diffusivity of hydrogen in steels followed a decreasing order of equiaxed ferrite and pearlite, AF, and bainite.

In the current study, the 0W steel consists mainly of polygonal ferrite and scattered pearlite, indicating the highest permeability and diffusivity compared to the W-containing steels. This is attributed to the ferrite/cementite interface in scattered pearlite and the grain boundaries of ferrite provide effective paths for hydrogen diffusion because a large amount of polygonal grains contribute to a large volume fraction of grain boundaries available as a hydrogen high diffusivity path [62]. As W is added, the amount of AF is increased. AF, which is characterised by short ferrite needles with a basket-weave feature, has randomly-oriented grain boundaries and high dislocation density due to tangled dislocations in it [65]. Hydrogen can be trapped reversibly at the tangled dislocations and then induces decrease in permeability and diffusivity of hydrogen in the steel. As reported in our previous work [14], the interlamellar spacing of pearlite decreases significantly after W addition. For the W-containing steels, the relatively low permeability and diffusivity of hydrogen might also be contributed to the W-induced low interlamellar spacing of pearlite. The higher the amount of AF as the W content is increased, the lower the permeability and diffusivity of hydrogen are then expected. After 1% W is added, the microstructure consists of mixed AF and bainite. The lowest permeability and diffusivity of hydrogen in the 1W specimen should be attributed to the high dislocation density of bainite and the cementite that is precipitated between the ferrite fingers acting as an obstacle for hydrogen transport [62,64]. As a result, the pre-charged hydrogen concentration presents a decreasing trend with W under the same hydrogen charging current density, as shown in **Figs. 4 and 5**.

Wang et al [16] studied the tensile fracture behaviour of quenched-and-tempered AISI 4135 steel at 1450 MPa on both the smooth and notched specimens. They found that the notched specimens did not show general yielding before an abrupt fracture, and all the stress versus displacement curves were appeared as straight lines. In the current work however, all the notched 0W, 0.1W and 0.5W

specimens that are uncharged still present similar tensile behaviour to the smooth specimens which are all characterised by three distinct stages including elastic deformation, plastic deformation and fracture [15]. The 1W specimen exhibits an early fracture before the ultimate notch stress is reached. One of the reasons should be the microstructural characteristics that contribute to lower tensile strength of the studied steels, as presented in **Table 3** and **Fig. 2**. Ferrite has a body-centred cubic (BCC) crystal structure, in which there are 48 slip systems. Ferrite grains possess high ductility because dislocations can readily move and multiply to produce large permanent changes in shape of steel structures [66]. The 0W steel is mainly composed of PF and pearlite, and the dislocation density in this steel is very low relative to that in the W-containing steels. A low dislocation density will cause a reduced amount of hydrogen trapped at dislocations, and the hydrogen will not accumulate rapidly due to the relatively high mobility of hydrogen during tensile deformation. Therefore, the hydrogen-charged 0W specimen still shows obvious three-stage deformation behaviour due to the high ductility of PF and low density of dislocation in the matrix even though the ductility is reduced due to the HE susceptibility. Several studies have indicated that hydrogen facilitates the emission and motion of dislocations [67,68]. As the mobility of dislocation is enhanced, a decreased strength will be obtained during tensile deformation. The work of Lü et al [69] indicated that dislocation movement did not initiate when the studied steel was put into the hydrogen gas with a pressure of 0.1 MPa for 3 h. After remaining in the hydrogen gas for 6 h, however, hydrogen started to move as the charged hydrogen concentration was increased to a critical value. Therefore, hydrogen cannot facilitate the dislocation emission and motion until a critical hydrogen concentration is reached. The present work shows that the tensile strength of the 0W specimen decreases greatly even though only 0.16 mass ppm hydrogen (curve A1 in **Fig. 6a**) is charged. This decrease is thought to be attributed to the high hydrogen concentration in the specimen, and the critical hydrogen concentration has been reached.

W addition induces significant change in the microstructural constituents (**Fig. 2**). The precipitates are refined as the W content is increased from 0 to 1%, as shown in **Fig. 13**. At the same time,

dislocation density is significantly enhanced, resulting increased strength and decreased ductility [15]. Dislocations can act as effective traps for hydrogen, thereby reducing the mobility of hydrogen atoms. Therefore, the higher dislocation density of the W-added steels would be expected to allow slower diffusion of hydrogen during tensile tests. When a moving dislocation meets a precipitate, the dislocation most likely will lose the H proton to the irreversible trap. Several studies have indicated that fine precipitates are more effective for hydrogen trapping relative to the coarse ones [70,71]. Studies on precipitates have shown that the trapping capacity also depends on the lattice mismatch, i.e. whether the precipitated particles are coherent or incoherent [30,44]. The work of Lee and Lee [30] showed that the trap activation energy of hydrogen increased with increasing the precipitated incoherent particle size which is attributed to the changes of interfacial free energy. Therefore, the role of trapping upon hydrogen embrittlement is still not clear. Trapping might have a positive effect since the amount of diffusible hydrogen is strongly reduced. In the other hand however, trapping might be detrimental when hydrogen weakens the structural integrity, e.g. grain boundaries [17]. Hydrogen accumulation at locations of high triaxial stress such as precipitate/matrix interface, dislocations and grain boundaries may weaken Fe-Fe bonds [72]. It has been reported that HE increases with increasing the strength levels of various steels including microalloyed steel [73], maraging steel [74] and Cr-Mo steel [75]. These combined effects are expected to cause an early fracture as the W content is increased; and the higher the pre-charged hydrogen concentration, the more susceptible of HE is expected under the same W content, as shown in **Fig. 6**.

The current work has indicated that the width of ductile region in the vicinity of notch root shows a decreasing trend with W, and no ductile fractured region is observed on the 1W specimen. The fracture surface of the notched specimen exhibits different characterisations from that of a smooth tensile specimen tested in air which is characterised by ductile dimples throughout the fractured cross section [15]. One of the reasons should be the notch sensitivity of the tested material. Previous studies indicated that hydrogen was inclined to be accumulated at the notch root, and the hydrogen effect at

the vicinity of notch root was much severer than that in a smooth specimen condition [56,59]. This phenomenon has been confirmed by Wang et al [16] that fracture initiates in the vicinity of the notch root in a ductile mode for the notched specimens, and the area fraction of ductile region decreases with an increase of stress concentration factor. There is still a lot of debate on the hydrogen-induced degradation in steels, and several mechanisms have been proposed and discussed [76-78]. Among them, the decohesion theory and internal pressure theory have been adopted by many researchers in the investigation of HE in cast Fe-C steel [18], high-Mn steel [36], forged carbon steel [79], pipeline steel [80] and high strength steel [81] etc with a varying hydrogen concentration from 0 to 26 mass ppm. In the decohesion theory, the presence of hydrogen atoms weakens atomic bonding force. The quasi-cleavage fracture occurred after hydrogen charging has been found to be attributed to the decohesion of interface boundaries [36]. The internal pressure theory suggests that hydrogen atoms combine into hydrogen gas molecules at or near the interface of second phase particles (such as precipitates and cementite) and metallic matrix. The hydrogen molecules cause a pressure build-up and induce microcracks. The hydrogen concentration that pre-charged under current density of 1 A/m² should be not high enough to form an sufficient internal pressure that can promote the initiation of microcracks, and no microcracks are observed on the fractured surfaces, as shown in **Figs. 8 - 10**. As the hydrogen charging current density is increased from 1 to 10 A/m², the pressure build-up takes effect due to the high amount of pre-charged diffusible hydrogen in the steels, leading to microcracks occur, as observed in the 0.1W and 0.5W specimens (**Fig. 12a - d**). Therefore, there is a critical hydrogen concentration that may cause the occurrence of microcracks. For the hydrogen-charged 0W and 1W specimens however, no microcracks are observed under the current density of 10 A/m². In the 0W specimen, the size of precipitates is coarse, and the interlamellar spacing of pearlite is large [14]; the hydrogen trapping capability is expected to be low relative to the W-added specimens. It is assumed that the accumulated hydrogen at the interface of precipitate/matrix and cementite/matrix is not high enough due to the coarse precipitated particles, large interlamellar spacing of pearlite, and as well as few dislocations which can act as hydrogen traps and transport during the notch tensile test.

Therefore, microcracks are not initiated in the 0W specimen. A full cleavage fracture should have occurred before enough internal pressure is formed to cause microcracks due to the poor plasticity of the 1W specimen since a certain time is required for hydrogen accumulation at the interfaces of precipitate/matrix and cementite/matrix.

Based on the aforementioned analysis and discussion, it can be concluded that microstructural features including dislocations, grain boundaries, precipitates and interlamellar spacing of pearlite may act as reversible and/or irreversible hydrogen traps in the steel to reduce the mobility of hydrogen towards regions of stress concentration ahead of the crack tip and thereby affect the susceptibility of HE and the fracture modes. When the hydrogen concentration in the traps increases above the critical value for crack initiation, the traps will act as crack initiation sites. Fine precipitates and low interlamellar spacing of pearlite can have positive and negative effects on the HE susceptibility of steels. In the one hand, fine precipitates and low interlamellar spacing of pearlite are more effective for hydrogen trapping, and can reduce the HE susceptibility [35]. In the other hand however, hydrogen trapping at fine precipitates and cementite may weaken the precipitate/matrix, cementite/matrix and Fe-Fe atomic bonding forces. When W is added in the microalloyed steels, the size of precipitates is refined, and the interlamellar spacing is reduced; at the same time the dislocation density is increased. With an increase of dislocation density after W addition, the amount of reversible hydrogen trapped at dislocations increases. The rate and amount of hydrogen accumulated at precipitate/matrix and cementite/matrix interfaces become high due to the losing of massive reversible hydrogen from the large amount of dislocations when they meet precipitates and cementite during notch tensile test. As a result, the hydrogen-induced embrittlement will be caused due to the aforementioned decohesion and internal pressure effects. The higher the W content, the finer the precipitates, the lower the interlamellar spacing, and the higher the dislocation density are obtained, and correspondingly the more susceptible of HE is expected.

5. Conclusions

- (1) The TDS analysis shows that an additional hydrogen desorption peak appears at the temperature of about 360 K for the 0W steel after hydrogen charging. The hydrogen desorption peak decreases gradually with the increase of W, and the peak shifts to a higher temperature side as W is added.
- (2) W addition decreases the amount of diffusible hydrogen in microalloyed steels under the same hydrogen charging current density. It is more difficult for hydrogen to permeate in the W-containing steels during hydrogen charging relative to the steel without W addition. W addition induces increased activation energy of hydrogen desorption.
- (3) Before hydrogen charging, the 0W, 0.1W and 0.5W steels exhibit a ductile fracture mode in the vicinity of notch root, and the area of ductile region decreases with increasing the W content. A full cleavage fracture is observed in the uncharged 1W steel. Hydrogen charging does not show noticeable effect on the fracture mode in the central zone.
- (4) Hydrogen charging benefits the ductile to quasi-cleavage fracture transition, and thus promotes the occurrence of embrittlement in microalloyed steels. High current density (10 A/m^2 in this study) leads to the occurrence of microcracks along the margin of the notch root of the 0.1W and 0.5W steels, while no microcracks are found in the 0W and 1W steels. The change of microstructure after W addition affects the occurrence of microcracks during notch tensile tests.
- (5) Microstructural features including dislocations, grain boundaries, precipitates and interlamellar spacing of pearlite affect the HE behaviours and fracture modes of microalloyed steels. The hydrogen-induced embrittlement in the studied microalloyed steels is thought to be caused by the combined effects of decohesion and internal pressure in the presence of hydrogen.

References

- [1] B.K. Show, R. Veerababu, R. Balamuralikrishnan, G. Malakondaiah, Effect of vanadium and titanium modification on the microstructure and mechanical properties of a microalloyed HSLA steel, *Mater. Sci. Eng. A* 527 (2010) 1595-1604.
- [2] J. Zhao, Z. Jiang, J.S. Kim, C.S. Lee, Effects of tungsten on continuous cooling transformation characteristics of microalloyed steels, *Mater. Des.* 49 (2013) 252-258.
- [3] J. Zhao, Z. Jiang, C.S. Lee, Effect of tungsten addition and heat treatment conditions on microstructure and mechanical properties of microalloyed forging steels, *Mater. Sci. Eng. A* 562 (2013) 144-151.
- [4] J. Zhao, Z. Jiang, C.S. Lee, Enhancing impact fracture toughness and tensile properties of a microalloyed cast steel by hot forging and post-forging heat treatment processes, *Mater. Des.* 47 (2013) 227-233.
- [5] J. Zhao, J.H. Lee, Y.W. Kim, Z. Jiang, C.S. Lee, Enhancing mechanical properties of a low-carbon microalloyed cast steel by controlled heat treatment, *Mater. Sci. Eng. A* 559 (2013) 427-435.
- [6] S.H. Mousavi Anijdan, D. Sediako, S. Yue, Optimization of flow stress in cool deformed Nb-microalloyed steel by combining strain induced transformation of retained austenite, cooling rate and heat treatment, *Acta Mater.* 60 (2012) 1221-1229.
- [7] M.L.N. da Silva, W. Regone, S.T. Button, Microstructure and mechanical properties of microalloyed steel forgings manufactured from cross-wedge-rolled preforms, *Scripta Mater.* 54 (2006) 213-217.
- [8] S.B. Kim, K.W. Paik, Y.G. Kim, Effect of Mo substitution by W on high temperature embrittlement characteristic in duplex stainless steels, *Mater. Sci. Eng. A* 247 (1998) 67-74.
- [9] J.I. Suk, C.N. Park, S.H. Hong, Y.G. Kim, Development and properties of tungsten-bearing stainless maraging steels, *Mater. Sci. Eng. A* 138 (1991) 367-273.

- [10] T. Narita, S. Ukai, S. Ohtsuka, M. Inoue, Effect of tungsten addition on microstructure and high temperature strength of 9CrODS ferritic steel, *J Nucl. Mater.* 417 (2011) 158-161.
- [11] S.G. Hong, W.B. Lee, C.G. Park, The effects of tungsten addition on the toughness of modified 9Cr-Mo steels, *Scripta Mater.* 43 (2000) 181-186.
- [12] W.J. Nam, C.S. Lee, D.Y. Ban, Improvement of sag resistance by the addition of tungsten in Si-Cr-Mo-V steels, *Scripta Mater.* 36 (1997) 1315-1320.
- [13] J.S. Park, S.J. Kim, C.S. Lee, Effect of W addition on the low cycle fatigue behavior of high Cr ferritic steels, *Mater. Sci. Eng. A* 298 (2001) 127-136.
- [14] J. Zhao, Y.W. Kim, J.H. Lee, J.M. Lee, H.S. Chang, C.S. Lee, Effect of tungsten addition on the mechanical properties and corrosion resistance of S355NL forging steel, *Met. Mater. Int.* 18 (2012) 217-223.
- [15] J. Zhao, T. Lee, J.H. Lee, Z. Jiang, C.S. Lee, Effects of tungsten addition on the microstructure and mechanical properties of microalloyed forging steels, *Metall. Mater. Trans. A* 44A (2013) 3511-3523.
- [16] M. Wang, E. Akiyama, K. Tsuzaki, Effect of hydrogen on the fracture behavior of high strength steel during slow strain rate test, *Corros. Sci.* 49 (2007) 4081-4097.
- [17] T. Michler, M.P. Balogh, Hydrogen environment embrittlement of an ODS RAF steel - Role of irreversible hydrogen trap sites, *Int. J. Hydrogen Energy* 35 (2010) 9746-9754.
- [18] D. Pérez Escobar, T. Depover, E. Wallaert, L. Duprez, M. Verhaege, K. Verbeken, Thermal desorption spectroscopy study of the interaction between hydrogen and different microstructural constituents in lab cast Fe-C alloys, *Corros. Sci.* 65 (2012) 199-208.
- [19] T. Michler, J. Naumann, Microstructural aspects upon hydrogen environment embrittlement of various bcc steels, *Int. J. Hydrogen Energy* 35 (2010) 821-832.
- [20] A.J. Slifka, E.S. Drexler, N.E. Nanninga, Y.S. Levy, J.D. McColskey, R.L. Amaro, et al., Fatigue crack growth of two pipeline steels in a pressurized hydrogen environment, *Corros. Sci.* 78 (2014) 313-321.

- [21] M. Javidi, S.B. Horeh, Investigating the mechanism of stress corrosion cracking in near-neutral and high pH environments for API 5L X52 steel, *Corros. Sci.* 80 (2014) 213-220.
- [22] G. Wang, Y. Yan, J. Li, J. Huang, Y. Su, L. Qiao, Hydrogen embrittlement assessment of ultra-high strength steel 30CrMnSiNi2, *Corros. Sci.* 77 (2013) 273-280.
- [23] M. Koyama, E. Akiyama, T. Sawaguchi, K. Ogawa, I.V. Kireeva, Y.I. Chumlyakov, et al., Hydrogen-assisted quasi-cleavage fracture in a single crystalline type 316 austenitic stainless steel, *Corros. Sci.* 75 (2013) 345-353.
- [24] Q. Liu, B. Irwanto, A. Atrens, The influence of hydrogen on 3.5NiCrMoV steel studied using the linearly increasing stress test, *Corros. Sci.* 67 (2013) 193-203.
- [25] S. Zheng, Y. Qi, C. Chen, S. Li, Effect of hydrogen and inclusions on the tensile properties and fracture behaviour of A350LF2 steels after exposure to wet H₂S environments, *Corros. Sci.* 60 (2012) 59-68.
- [26] H.F. Jackson, K.A. Nibur, C. San Marchi, J.D. Puskar, B.P. Somerday, Hydrogen-assisted crack propagation in 304L/308L and 21Cr-6Ni-9Mn/308L austenitic stainless steel fusion welds, *Corros. Sci.* 60 (2012) 136-144.
- [27] M. Koyama, E. Akiyama, K. Tsuzaki, Effect of hydrogen content on the embrittlement in a Fe-Mn-C twinning-induced plasticity steel, *Corros. Sci.* 59 (2012) 277-281.
- [28] M. Koyama, E. Akiyama, K. Tsuzaki, Hydrogen embrittlement in a Fe-Mn-C ternary twinning-induced plasticity steel, *Corros. Sci.* 54 (2012) 1-4.
- [29] A. Mustapha, E.A. Charles, D. Hardie, Evaluation of environment-assisted cracking susceptibility of a grade X100 pipeline steel, *Corros. Sci.* 54 (2012) 5-9.
- [30] S.M. Lee, J.Y. Lee, The effect of the interface character of TiC particles on hydrogen trapping in steel, *Acta Metall.* 35 (1987) 2659-2700.
- [31] J.S. Kim, Y.H. Lee, D.L. Lee, K.T. Park, C.S. Lee, Microstructural influences on hydrogen delayed fracture of high strength steels, *Mater. Sci. Eng. A* 505 (2009) 105-110.
- [32] X. Yuan, Precipitates and hydrogen permeation behavior in ultra-low carbon steel, *Mater. Sci.*

Eng. A 452-453 (2007) 116-120.

- [33] K. Kiuchi, R.B. McLellan, The solubility and diffusivity of hydrogen in well-annealed and deformed iron, *Acta Metall.* 31 (1983) 961-984.
- [34] W.Y. Choo, J.Y. Lee, Thermal analysis of trapped hydrogen in pure iron, *Metall. Trans. A* 13A (1982) 135-140.
- [35] H.J. Kang, J.S. Yoo, J.T. Park, S.T. Ahn, N. Kang, K.M. Cho, Effect of nano-carbide formation on hydrogen-delayed fracture for quenching and tempering steels during high-frequency induction heat treatment, *Mater. Sci. Eng. A* 543 (2012) 6-11.
- [36] Y.S. Chun, J.S. Kim, K.T. Park, Y.K. Lee, C.S. Lee, Role of ϵ martensite in tensile properties and hydrogen degradation of high-Mn steels, *Mater. Sci. Eng. A* 533 (2012) 87-95.
- [37] J.Y. Lee, J. L. Lee, A trapping theory of hydrogen in pure iron, *Philos. Mag. A*, 56 (1987) 293-309.
- [38] J.L. Lee, J.Y. Lee, Identification of defects generated during cathodic charging in pure iron by thermal analysis technique, *Metall. Trans. A* 16A (1985) 468-471.
- [39] I. Maroef, Hydrogen trapping in ferritic steel weld metal, *Int. Mater. Rev.* 47(4) (2002) 191-223.
- [40] R.A. Oriani, J.P. Hirth, M. Smialowski, *Hydrogen Degradation of Ferrous Alloys*, Noyes Publications, UK, 1985.
- [41] K.Y. Lee, J.Y. Lee, D.R. Kim, A study of hydrogen-trapping phenomena in AISI 5160 spring steel, *Mater. Sci. Eng.* 67 (1984) 213-220.
- [42] J.L. Lee, J.Y. Lee, Hydrogen trapping in AISI 4340 steel, *Met. Sci.* 17 (1983) 426-432.
- [43] J.L. Lee, J.Y. Lee, The interaction of hydrogen with the interface of Al_2O_3 particles in iron, *Metall. Trans. A* 17A (1986) 2183-2186.
- [44] F.G. Wei, K. Tsuzaki, Quantitative analysis on hydrogen trapping of TiC particles in steel, *Metall. Mater. Trans. A* 37A (2006) 331-353.
- [45] G.M. Pressouyre, I.M. Bernstein, A quantitative analysis of hydrogen trapping, *Metall. Trans. A* 9A (1978) 1571-1580.

- [46] I.J. Park, K.H. Jeong, J.G. Jung, C.S. Lee, Y.K. Lee, The mechanism of enhanced resistance to the hydrogen delayed fracture in Al-added Fe-18Mn-0.6C twinning-induced plasticity steels, *Int. J. Hydrogen Energy* 37 (2012) 9925-9932.
- [47] J. Sojka, V. Vodárek, I. Schindler, C. Ly, M. Jérôme, P. Váňová, et al., Effect of hydrogen on the properties and fracture characteristics of TRIP 800 steels, *Corros. Sci.* 53 (2011) 2575-2581.
- [48] A.M Elhoud, N.C. Renton, W.F. Deans, Hydrogen embrittlement of super duplex stainless steel in acid solution, *Int. J. Hydrogen Energy* 35 (2010) 6455-6464.
- [49] L. Marchetti, E. Herms, P. Laghoutaris, J. Chêne, Hydrogen embrittlement susceptibility of tempered 9%Cr-1% Mo steel, *Int. J. Hydrogen Energy* 36 (2011) 15880-15887.
- [50] L.W. Tsay, M.Y. Chi, Y.F. Wu, J.K. Wu, D.-Y. Lin, Hydrogen embrittlement susceptibility and permeability of two ultra-high strength steels, *Corros. Sci.* 48 (2006) 1926-1938.
- [51] B. Beidokhti, A. Dolati, A.H. Koukabi, Effects of alloying elements and microstructure on the susceptibility of the welded HSLA steel to hydrogen-induced cracking and sulphide stress cracking, *Mater. Sci. Eng. A* 507 (2009) 167-173.
- [52] W.K Kim, S.U. Koh, B.Y. Yang, K.Y. Kim, Effect of environmental and metallurgical factors on hydrogen induced cracking of HSLA steels, *Corros. Sci.* 50 (2008) 3336-3342.
- [53] S.J. Kim, H.G. Jung, K.Y. Kim, Effect of post-weld heat treatment on hydrogen-assisted cracking behaviour of high-strength process pipe steel in a sour environment, *Scripta Mater.* 67 (2012) 895-898.
- [54] N.E. Nanninga, Y.S. Levy, E.S. Drexler, R.T. Condon, A.E. Stevenson, A.J. Slifka, Comparison of hydrogen embrittlement in three pipeline steels in high pressure gaseous hydrogen environments, *Corros. Sci.* 59 (2012) 1-9.
- [55] T. Alp, F. I. Iskanderani, A.H. Zahed, Hydrogen effects in a dual-phase microalloy steel, *J. Mater. Sci.* 26 (1991) 5644-5654.
- [56] D. Hardie, Su'e Liu, The effect of stress concentration on hydrogen embrittlement of a low alloy steel, *Corros. Sci.* 38 (1996) 721-733.

- [57] L.W. Tsay, W.C. Lee, W.C. Luu, J.K. Wu, Effect of hydrogen environment on the notched tensile properties of T-250 maraging steel annealed by laser treatment, *Corros. Sci.* 44 (2002) 1311-1327.
- [58] E. Proverbio, P. Longo, Sub critical crack growth in hydrogen assisted cracking of cold drawn eutectoid steel, *Corros. Sci.* 49 (2007) 2421-2435.
- [59] M. Wang, E. Akiyama, K. Tsuzaki, Effect of hydrogen and stress concentration on the notch tensile strength of AISI 4135 steel, *Mater. Sci. Eng. A* 398 (2005) 37-46.
- [60] H.E. Kissinger, Reaction kinetics in differential thermal analysis, *Anal. Chem.* 29 (1957) 1702-1706.
- [61] F.G. Wei, T. Hara, K. Tsuzaki, Precise determination of the activation energy for desorption of hydrogen in two Ti-added steels by a single thermal-desorption spectrum, *Metall. Mater. Trans. B* 35B (2004) 587-597.
- [62] W.C. Luu, J.K. Wu, The influence of microstructure on hydrogen transport in carbon steels, *Corros. Sci.* 38 (1996) 239-245.
- [63] N. Parvathavarthini, S. Saroja, R.K. Dayal, H.S. Khatak, Studies on hydrogen permeability of 2.25% Cr-1% Mo ferritic steel: correlation with microstructure, *J. Nucl. Mater.* 288 (2001) 187-196.
- [64] S.H. Wang, W.C. Luu, K.F. Ho, J.K. Wu, Hydrogen permeation in a submerged arc weldment of TMCP steel, *Mater. Chem. Phys.* 77 (2002) 447-454.
- [65] G.T. Park, S.U. Koh, H.G. Jung, K.Y. Kim, Effect of microstructure on the hydrogen trapping efficiency and hydrogen induced cracking of linepipe steel, *Corros. Sci.* 50 (2008) 1865-1871.
- [66] G. Krauss, *Steels: Processing, Structure, and Performance*, ASM International, Ohio, 2005.
- [67] S. Taketomi, R. Matsumoto, N. Miyazaki, Atomistic study of the effect of hydrogen on dislocation emission from a mode II crack tip in alpha iron, *Int. J. Mech. Sci.* 52 (2010) 334-338.
- [68] P.J. Ferreira, I.M. Robertson, H.K. Birnbaum, Hydrogen effects on the interaction between dislocations, *Acta Mater.* 46 (1998) 1749-1757.

- [69] H. Lü, M. Li, T. Zhang, W. Chu, Hydrogen-enhanced dislocation emission, motion and nucleation of hydrogen-induced cracking for steel, *Sci. China (Ser. E)* 40 (1997) 530-538.
- [70] E. Ramírez, J.G. González-Rodríguez, A. Torres-Islas, S. Serna, B. Campillo, G. Dominguez-Patiño, et al., Effect of microstructure on the sulphide stress cracking susceptibility of a high strength pipeline steel, *Corros. Sci.* 50 (2008) 3534-3541.
- [71] M.C. Zhao, M. Liu, A. Atrens, Y.Y. Shan, K. Yang, Effect of applied stress and microstructure on sulfide stress cracking resistance of pipeline steels subject to hydrogen sulfide, *Mater. Sci. Eng. A* 478 (2008) 43-47.
- [72] R.A. Oriani, Hydrogen-the versatile embrittler, *Corros.* 43 (1987) 390-397.
- [73] A. Torres-Islas, S. Serna, B. Campillo, J. Colin, A. Molina, Hydrogen embrittlement behavior on microalloyed pipeline steel in NS-4 solution, *Int. J. Electrochem. Sci.* 8 (2013) 7608-7624.
- [74] L.W. Tsay, H.L. Lu, C. Chen, The effect of grain size and aging on hydrogen embrittlement of a maraging steel, *Corros. Sci.* 50 (2009) 2506-2511.
- [75] M. Imade, S. Fukuyama, L. Zhang, M. Wen, K. Yokogawa, Hydrogen environment embrittlement of SCM440 steel in high pressure hydrogen at room temperature, *J. Jpn. Inst. Met.* 69 (2005) 190-193.
- [76] H.K. Birnbaum, P. Sofronis, Hydrogen-enhanced localized plasticity - a mechanism for hydrogen-related fracture, *Mater.Sci. Eng. A* 176 (1994) 191-202.
- [77] M. Nagumo, Function of hydrogen in embrittlement of high-strength steels, *ISIJ Int.* 41 (2001) 590-598.
- [78] J.P. Hirth, Effects of hydrogen on the properties of iron and steel, *Metall. Trans. A* 11A (1980) 861-890.
- [79] Y. Qi, H. Luo, S. Zheng, C. Chen, D. Wang, Effect of immersion time on the hydrogen content and tensile properties of A350LF2 steel exposed to hydrogen sulphide environments, *Corros. Sci.* 69 (2013) 164-174.
- [80] R. Wang, Effects of hydrogen on the fracture toughness of a X70 pipeline steel, *Corros. Sci.* 51

(2009) 2803-2810.

- [81] N.R. Raykar, R.K. Singh Raman, S.K. Maiti, L. Choudhary, Investigation of hydrogen assisted cracking of a high strength steel using circumferentially notched tensile test, Mater. Sci. Eng. A 547 (2012) 86-92.

Figure Captions:

Fig. 1. Dimensions (in mm) and appearance of a notched specimen for the SSRT.

Fig. 2. Microstructures of the (a) 0W, (b) 0.1W, (c) 0.5W and (d) 1W steels.

Fig. 3. Hydrogen desorption curves of the 0W steel with (a) heating rate of 100 K/h and (b) current density of 10A/m².

Fig. 4. Effects of W on the profile of hydrogen desorption curves under the hydrogen charging current density of 5 A/m² and heating rate of 100 K/h.

Fig. 5. Dependence of hydrogen concentration on charging current density.

Fig. 6. Notch tensile curves of the (a) 0W, (b) 0.1W, (c) 0.5W and (d) 1W steels charged under different current densities.

Fig. 7. Dependence of (a) σ_f and (b) D_f on W content.

Fig. 8. Fracture surfaces of the 0W specimens that were (a,c,e) uncharged and (b,d,f) hydrogen-charged under current density of 1 A/m².

Fig. 9. Fracture surfaces of the (a,b) 0.1W and (c,d) 0.5W specimens: (a,c) uncharged, and (b,d) hydrogen-charged under current density of 1 A/m².

Fig. 10. Fracture surfaces of the 1W specimens that were (a) uncharged and (b) hydrogen-charged under current density of 1 A/m².

Fig. 11. Fracture surfaces of the 0W specimen that is hydrogen-charged under current density of 10 A/m².

Fig. 12. Fracture surfaces of the (a,b) 0.1W, (c,d) 0.5W and (e,f) 1W specimens that were hydrogen-charged under current density of 10 A/m².

Fig. 13. Characteristics of the precipitates in the (a) 0W and (b) 1W steels.

Table Captions:

Table 1 Trapping activation energies for various trapping sites in iron and steels

Table 2 Chemical compositions of the investigated steels (wt.%)

Table 3 Mechanical properties of the investigated steels

Fig. 1. Dimensions (in mm) and appearance of a notched specimen for the SSRT.

Fig. 2. Microstructures of the (a) 0W, (b) 0.1W, (c) 0.5W and (d) 1W steels.

Fig. 3. Hydrogen desorption curves of the 0W steel with (a) heating rate of 100 K/h and (b) current density of 10 A/m^2 .

Fig. 4. Effects of W on the profile of hydrogen desorption curves under the hydrogen charging current density of 5 A/m^2 and heating rate of 100 K/h .

Fig. 5. Dependence of hydrogen concentration on charging current density.

Fig. 6. Notch tensile curves of the (a) 0W, (b) 0.1W, (c) 0.5W and (d) 1W steels charged under different current densities.

Fig. 7. Dependence of (a) σ_f and (b) D_f on W content.

Fig. 8. Fracture surfaces of the 0W specimens that were (a,c,e) uncharged and (b,d,f) hydrogen-charged under current density of 1 A/m^2 .

Fig. 9. Fracture surfaces of the (a,b) 0.1W and (c,d) 0.5W specimens: (a,c) uncharged, and (b,d) hydrogen-charged under current density of 1 A/m².

Fig. 10. Fracture surfaces of the 1W specimens that were (a) uncharged and (b) hydrogen-charged under current density of 1 A/m^2 .

Fig. 11. Fracture surfaces of the 0W specimen that is hydrogen-charged under current density of 10 A/m^2 .

Fig. 12. Fracture surfaces of the (a,b) 0.1W, (c,d) 0.5W and (e,f) 1W specimens that were hydrogen-charged under current density of 10 A/m^2 .

Fig. 13. Characteristics of the precipitates in the (a) 0W and (b) 1W steels.

Table 1 Trapping activation energies for various trapping sites in iron and steels

Trapping sites	Trapping activation energy (kJ/mol)	Reference
<i>Reversible trapping sites:</i>		
Iron lattice	5.4-7.1	[33]
Grain boundary	17.2-18.6	[34,35]
Austenite/martensite interface	22	[36]
Dislocation	26.4-26.8	[34,37]
Austenite/dislocation boundary	37	[36]
Microvoid	35.2-40	[34,38]
Fe oxide interface	47	[17,39]
<i>Irreversible trapping sites:</i>		
Ferrite/cementite interface	66.3-68.4	[16,31]
Cr carbide interface	67	[40]
Y ₂ O ₃ interface	70	[39]
MnS interface	72	[41,42]
Al ₂ O ₃ interface	79-86.2	[41,43]
Fe ₃ C interface	84	[39]
TiC interface	68-137	[44,45]

Table 2 Chemical compositions of the investigated steels (wt.%)

Steels	C	Mn	Cr	Ni	Cu	Si	Al	V	Nb	Ti	P	S	N	W
0W	0.171	1.22	0.103	0.025	0.023	0.469	0.019	0.015	0.023	0.019	0.013	0.008	0.007	0
0.1W	0.170	1.20	0.103	0.024	0.024	0.471	0.024	0.015	0.023	0.020	0.014	0.009	0.008	0.09
0.5W	0.167	1.20	0.113	0.021	0.022	0.497	0.024	0.014	0.018	0.023	0.008	0.008	0.005	0.47
1W	0.171	1.20	0.112	0.024	0.022	0.499	0.021	0.016	0.020	0.020	0.008	0.008	0.006	0.99

Table 3 Mechanical properties of the investigated steels

Steels	YS (MPa)	UTS (MPa)	Strain (%)	Hardness (HV2)
0W	299.1	585.6	31.2	185
0.1W	313.4	624.9	29.2	217
0.5W	345.7	668.2	28.3	223
1W	351.9	711.1	24.9	232

YS: yield strength; and UTS: ultimate tensile strength.